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SUMMARY REPORT NO. 1

2 OCTOBER 1960

TO

2 DECEMBER 1961

SN106, 749

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GEORGE C. MARSHALL SPACE FLIGHT CENTER
HUNTSVILLE, ALABAMA

CONTRACT NO. NAS 8-50

DEVELOPMENT OF CERAMIC FIBERS FOR REINFORCEMENT IN COMPOSITE MATERIALS

L. E. GATES, W. E. LENT AND W. T. TEAGUE

15 DECEMBER 1961

HUGHES

HUGHES AIRCRAFT COMPANY

REV 2/84

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I. SUMMARY

Refinements of the vertical arc fiberizing apparatus resulted in its ability to fiberize very different refractory glasses having wide ranges of properties. Although the apparatus was originally designed as a laboratory research tool for the evaluation of many compositions daily, up to 1/4 pound of fibers of a single composition could be produced in an 8-hour day. Fibers up to 6-1/2 feet long were produced with the apparatus.

Studies were conducted of two methods of fiberizing refractory glasses requiring rapid freezing from the melt. The first method consisted of fiberizing droplets of molten glass passing through an annular nozzle. The second method consisted of reconstructing the annular nozzle in the shape of a horseshoe to achieve a shorter delay in blasting a molten droplet from the tip of a rod. Both methods were judged feasible for producing fibers of glasses requiring rapid freezing. The first method would be more amenable to volume fiber production.

Studies of induction heating for fiber formation did not lead to its designation as a very efficient heating method. Problems remain to be solved in the design of a suitable susceptor for a higher heating rate, in protecting the susceptor from oxidation with an inert gas, in contamination of the melt from a refractory crucible, and in the protective radiation shielding of the induction concentrator coil. It is not considered practical to continue studies of this heating method.

In the course of this program 151 refractory glass compositions were evaluated for fiber forming characteristics. Of the various types of materials studied, the following showed promise in producing acceptable refractory fibers: silica-spinel (magnesium aluminate), silica-spinel-zirconia, silica-zirconia, silica-zinc spinel, aluminum phosphate glasses, and fluoride glasses. Compositions which did not produce acceptable fibers were high zirconia materials, barium spinels, and calcium aluminates.

Improvements in the testing apparatus for single fiber tensile strength increased the precision of tests conducted on nine fibers. The highest mean tensile strength, a value of 295,000 psi, was obtained with

R-141 fibers. Treatment of R-74 fibers with anhydrous Linde A-1100 silane finish improved its mean fiber tensile strength by 25 percent. The lapse of time after fiber formation had no measurable effect on tensile strength.

A static heating test conducted with various high melting fibers indicated that Fiberfrax and R-108 underwent no significant changes in bulk volume or resiliency on exposure to 2750°F (1510°C) in an oxidizing atmosphere.

For fiber-resin composition fabrication, ten fiber materials were selected on the bases of high fiber yield, fusion temperature, and type of composition. Fiberfrax, a commercial ceramic fiber, was included for comparison.

A new, more effective method of removing pellets from blown fibers was developed. The depelletized fibers were treated with a silane finish and felted into ten-inch diameter felts prior to resin impregnation. Composites containing 30 percent by weight of CTL 91-LD phenolic resin were molded under high pressure from the impregnated felts and post-cured to achieve optimum properties.

Flexural strength, flexural modules of elasticity, and punch shear strength tests were conducted on the composite specimens. The highest average flexural strength obtained was 19,958 psi with the R-74 fiber-resin composite. This compares very favorably with the military specification of 13,000 psi flexural strength for randomly oriented fiber reinforced composites. The highest punch shear strength (11,509 psi) was obtained with the R-89 fiber-resin composite. The effects of anhydrous fiber finishes on composite strength were not clearly indicated.

Plasma arc tests at a heat flux of 550 BTU/foot²-sec on eight composite materials indicated ablation rates generally equivalent to Fiberglas-Micarta No. 259-2. The composite reinforced with R-99 fibers had an average ablation rate of 0.008 inch per second and appears quite promising on the basis of these tests.

Preliminary studies for processing fibers into yarn and fabric were conducted with R-99 fibers. The use of certain organic gums aided in

fabricating by hand several relatively strong yarns and a crude fabric swatch. This indicated the practicality of developing techniques for processing these fibers into yarn and fabric without significant damage to the fibers.

II. PURPOSE

The purpose of Contract No. NAS8-50 is to conduct research directed toward the development of ceramic fibers and ceramic fiber composites for use in space technology. The work shall include but not be limited to the following:

1. Develop refractory glass compositions with characteristics suitable for fiber forming.
2. Develop methods for forming fibers from the above refractory glass compositions.
3. Study the pertinent fiber forming parameters for each promising composition as necessary to achieve reproducibility.
4. Conduct physical, mechanical, and thermal property tests and petrographic analysis on promising fibers.
5. Fabricate fiber-matrix composite test specimens and conduct physical, mechanical, and thermal property tests on these specimens.
6. Furnish specimens to MSFC of promising fibers and composites (organic or inorganic matrix as required) obtained as a result of the above.
7. Develop quantity production methods for fiber forming.
8. Develop inorganic matrix materials compatible with the ceramic fibers; prepare test specimens and conduct property tests on these specimens.
9. Ascertain the feasibility of ceramic fiber-composite materials for use in structures for cryogenic and hyperthermal applications.

III. EXPERIMENTAL WORK

A. Fiber Forming

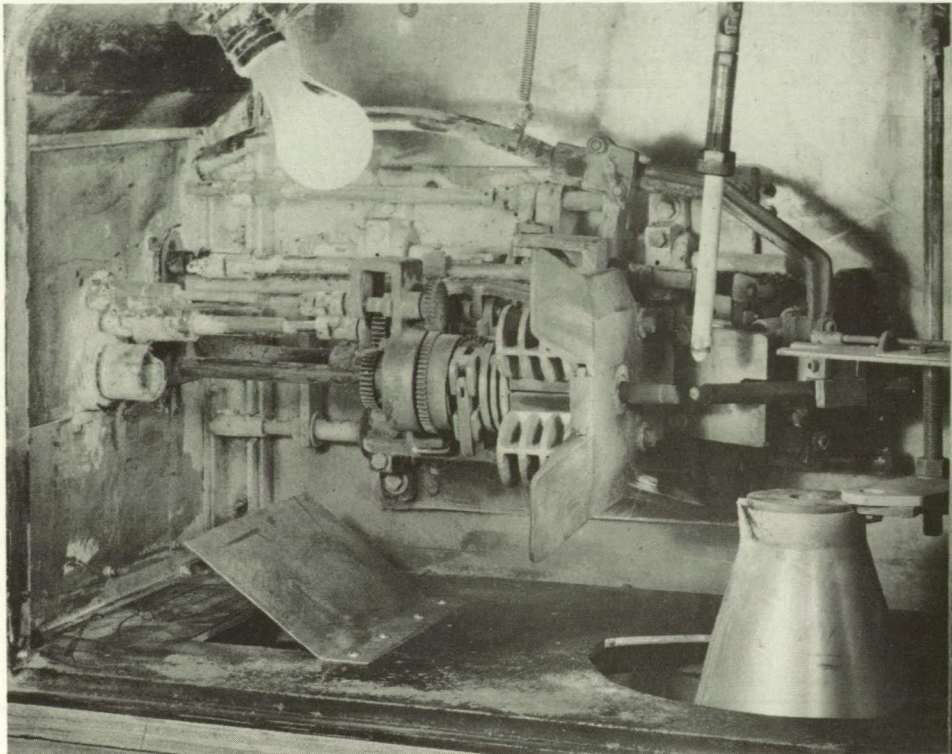
1. Vertical Arc Fiberizing

In the arc fiberizing apparatus a rod of material is fiberized by melting the tip in a high intensity d-c arc, removing it momentarily to cool, encircling the tip with an annular nozzle, and blasting fibers from the tip with high pressure gas jets. For uniform heating the rod is rotated in the arc by an electric motor. Timers are provided for automatic control of blast delay and blast duration and are adjustable over wide ranges to suit the fiberizing characteristics of different refractory glasses. Studies of various annular nozzle configurations, blast pressures, types of gases, and the operating parameters were effective in improving the fiber quality and yield and in increasing the operating efficiency. Although the apparatus was designed as a research tool for the evaluation of many compositions daily, with a single high yield material up to one-fourth pound of depelletized fibers could be produced in an eight-hour day, Figures 1 and 2.

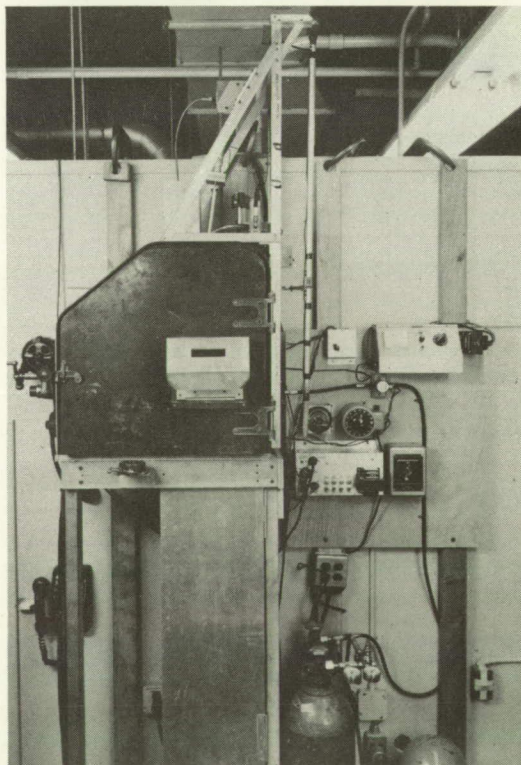
2. Continuous Fiberizing

Studies of several methods of continuous fiberizing were conducted using a 10-kva Lepel induction power supply to heat a refractory crucible. Initial studies consisted of heating various sizes of graphite rods in a water-cooled induction concentrator to determine the optimum power settings. Attempts were then made to melt various powdered refractory metal borides, carbides, and nitrides and also several glass compositions by self-induction. Even when these materials were heated to 1700°C with a gas flame, there was insufficient electrical conduction to generate internal heat by induction at the operating frequency of this power supply (100 kc).

Two heating methods utilizing a graphite susceptor were then evaluated. The first method consisted of heating the glass in air atmosphere in refractory crucibles into which close-fitting tubular or rod susceptors were inserted. The crucibles were made of boron nitride or of sintered material



Arc Apparatus Interior
and Ceramic Rod



Exterior Arrangement
and Controls

Figure 1. Vertical fiberizing apparatus.

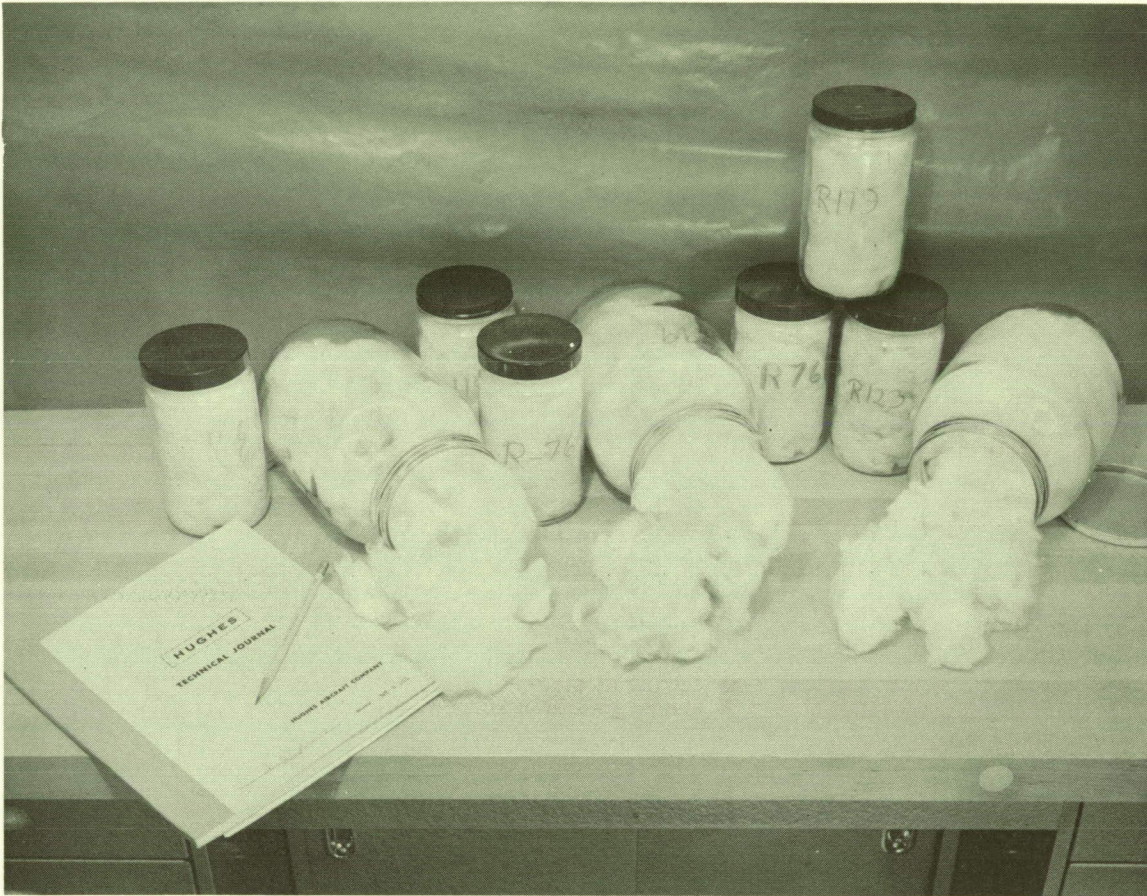
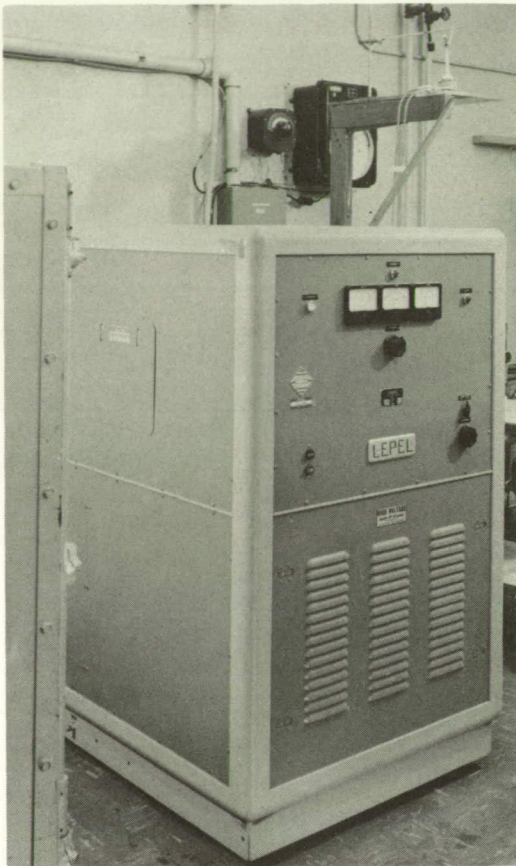


Figure 2. Fibers produced in arc apparatus.



Lepel Induction Generator

Induction Heating of
Ceramic Rod

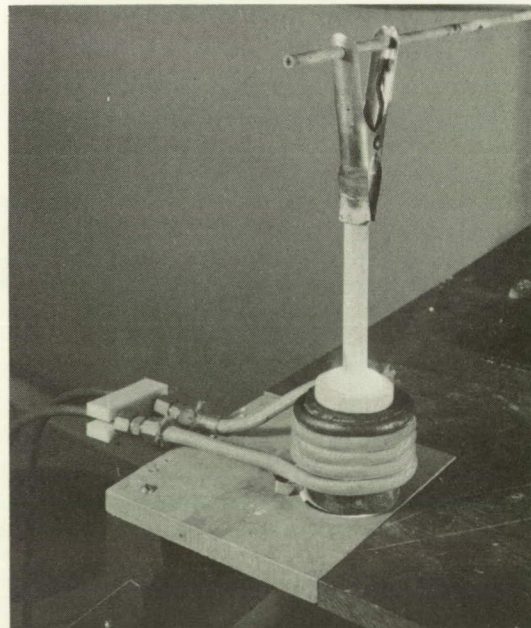


Figure 3. Induction heating.

of the glass to be evaluated. This method resulted in considerable carbon contamination of the glass from the graphite susceptor, whichever type of susceptor was tried. Also the boron nitride crucibles were heavily attacked by the molten glass.

The second heating method consisted of suspending a sintered rod of material in a tubular susceptor and heating it by radiation and convection. This method was highly successful, resulting in melting a fairly continuous stream of glass droplets from the tip of the rod as it was lowered into the susceptor. The glass droplets were completely free from carbon contamination. No attempt was made at that time to fiberize the falling droplets.

Several problems remain to be solved. The melting rate must be increased to provide a continuous stream for efficient fiberizing; radiation shielding must be utilized for protection of the induction concentrator and the susceptor must be protected from oxidation with an inert gas.

B. Ceramic Fiber Compositions

The work on 35 new compositions in the fourth quarter consisted of not only improving the yields and fusion temperatures of earlier compositions but also studies of new high temperature glass systems. The raw materials were processed into rods and fired according to the standard procedure previously established (Quarterly Report No. 2, pages 7 and 8).

Since the glass fiber fusion temperature was considered a major factor in the evaluation of new materials for further study, this property is listed along with other data on the fiberizing characteristics in Table I. The fusion temperatures were determined according to the ASTM test No. C24-46 for Pyrometric Cone Equivalent of Refractory Materials. In preparing the specimens, sufficient fibers of those compositions with yields greater than one gram per 50 blasts were pulverized into a fine powder to make a standard PCE cone. The use of the fibers rather than the raw composition constituents assured that any portion of the constituents

volatilized during arc fiberizing would not be present and the fusion temperatures would be those of the actual glasses composing the fibers. In several cases where no fibers were formed but glassy pellets suggested a glass-forming tendency, fusion temperatures of the pellets were determined. Since they are arc-melted, the pellets also would represent the true composition of a glass fiberized in the apparatus. (It is assumed that no further volatilization of a constituent will occur after a molten droplet is removed from the arc because of the sharp drop in temperature.)

1. Modifications of R-76: R-116 through R-125 and R-144 through R-148.

Studies were made of additions of various oxides to R-76 to lower the viscosity and increase the fiber yield without lowering the fusion temperature. Up to ten percent of fluxing oxides and a borosilicate glass frit were added. Additions of phosphorus pentoxide (R-117) and samarium oxide (R-123) were somewhat effective in lowering the viscosity and the replacement of magnesia with an increased amount of alumina (R-119) was very effective. These three materials and the composition containing CeO_2 (R-147) were the only materials with fiber yields high enough to justify further study. The yields of R-117 and R-123 were less than that of R-76 and the higher yields of R-119 and R-147 were achieved at the expense of a 30°C and a 105°C decrease in fusion temperatures, respectively.

2. Aluminum Phosphate Glasses: R-126 through R-133 and R-151.

This series of refractory aluminum phosphate glasses had fusion temperatures exceeding 1400°C . All of these materials formed clear, glassy pellets, but only the one containing silica (R-132) could be fiberized. Nevertheless, the effectiveness of phosphorus pentoxide as a high temperature glass former was definitely established. The main difficulty with these materials was the fragility of the rods after sintering. The viscosities of the glasses were low and relatively long delay times were

required before blasting. This characteristic would imply that they may be good candidates for fiberizing by an orifice method because of a long working range.

3. Calcium Aluminate Glasses: R-134 through R-139.

A series of high temperature calcium aluminate glasses were studied which consisted of combinations of calcium oxide, alumina, calcium silicate, and silica. The areas of low-melting calcium aluminate eutectics were avoided. The compositions evaluated were sufficiently refractory, but no fibers were formed, and no indication of glass forming tendency was observed.

4. Fluoride Glasses: R-140 through R-143 and R-149 and R-150.

A series of compositions was prepared to study the effects of partially substituting fluorine for oxygen in glass forming systems. Of the six compositions evaluated, three materials had satisfactory fiber yields. Compositions R-149 and R-150 had fusion temperatures of 1500° and 1520°C, respectively. Composition R-141, with a fusion temperature of 1530°C, contained no silica. It is apparent that under the proper conditions high temperature glass fibers containing no silica can be produced if a strong glass former is substituted. In this series calcium fluoride was substituted for calcium oxide for those materials containing silica; in R-141 the glass former was alumina with the calcium fluoride apparently acting separately as a modifier. It is believed by some investigators that the larger diameter of the fluorine anion (replacing oxygen) is responsible for its ability to act as a glass network former in that it promotes a greater state of disorder. Further studies of fluorides as partial replacements for oxides are recommended.

Composition Number	Material	Weight Percent	Optimum Blast Delay Time Seconds	Fiber Yield Grams per 50 Blasts	Comments	Fusion Temperature °C
R116	SiO ₂	54.5	0.5	0	Melted in 1400°C sinter	1505
	Al ₂ O ₃	6.8				
	MgO	2.3				
	ZrO ₂	27.2				
	Sb ₂ O ₃	9.2				
R117	SiO ₂	54.5	0.5	1.0	1-6 inch very glassy fibers	1505
	Al ₂ O ₃	6.8				
	MgO	2.3				
	ZrO ₂	27.2				
	P ₂ O ₅	9.2				
R118	SiO ₂	55.8	0.5	0	Melted in 1400°C sintering	1575
	Al ₂ O ₃	6.9				
	MgO	2.3				
	ZrO ₂	27.6				
	V ₂ O ₅	7.4				
R119	SiO ₂	60.0	0.5	3.4	Medium texture fibers, viscosity lower than R-76	1575
	Al ₂ O ₃	10.0				
	ZrO ₂	30.0				
R120	SiO ₂	70.0	0.5	0.8	Very viscous fibers similar to R76	
	Al ₂ O ₃	3.7				
	MgO	1.3				
	ZrO ₂	25.0				
R121	SiO ₂	60.0	0.5	0	Melted in 1400°C sintering	
	Al ₂ O ₃	7.5				
	MgO	2.5				
	ZrO ₂	25.0				
	LB-88*	5.0				
R122	SiO ₂	55.8	0.5	0	Melted in 1400°C sintering	
	Al ₂ O ₃	6.9				
	MgO	2.3				
	ZrO ₂	27.6				
	CoO ₂	7.4				
R123	SiO ₂	58.2	0.5	2.2	1-3 inch fine textured fibers pink color	1575
	Al ₂ O ₃	7.3				
	MgO	2.4				
	ZrO ₂	29.2				
	Sa ₂ O ₃	2.9				
R124	SiO ₂	54.5	0.5	0.2	Low viscosity very fine short fibers	
	Al ₂ O ₃	6.8				
	MgO	2.3				
	ZrO ₂	27.2				
	SnO ₂	9.2				
R125	SiO ₂	54.5	0.5	0	Melted in 1400°C sinter	
	Al ₂ O ₃	6.8				
	MgO	2.3				
	ZrO ₂	27.2				
	TiO ₂	9.2				
R126	Al ₂ O ₃	42.0	0.5	0	Rods too fragile	
	P ₂ O ₅	58.0				
R127	Al ₂ O ₃	36.0	0.5	0	Rapid solidification, some glassy pellets	
*Glass frit from Glastex Chemical Co., Los Angeles, California.						

Table I. Ceramic fiber compositions.

Composition Number	Material	Weight Percent	Optimum Blast Delay Time Seconds	Fiber Yield Grams per 50 Blasts	Comments	Fusion Temperature °C
R128	Al ₂ O ₃	30.0		0	Rods too fragile	
	P ₂ O ₅	70.0				
R129	Al ₂ O ₃	70.0		0	Rods too fragile	
	P ₂ O ₅	30.0				
R130	Al ₂ O ₃	90.0		0	Rods too fragile	
	P ₂ O ₅	10.0				
R131	Al ₂ O ₃	34.0	2.0	0.4	1-3 inch fine fibers, rods fragile	
	P ₂ O ₅	46.0				
	SiO ₂	20.0				
R132	Al ₂ O ₃	40.0	1.0	1.2	1-3 inch fine fibers	1790
	P ₂ O ₅	15.0				
	SiO ₂	45.0				
R133	Al ₂ O ₃	77.2	3.0	0.2	Very fine clean fibers	1740*
	P ₂ O ₅	2.6				
	CaO	20.2				
R134	Al ₂ O ₃	30.0		0	Rods dis-integrated	
	CaO	70.0				
R135	Al ₂ O ₃	85.0		0	No fibers; hexagonal crystals	1840*
	CaO	15.0				
R136	Al ₂ O ₃	24.0		0	Rods dis-integrated in 1400°C sinter	
	CaO	56.0				
	SiO ₂	20.0				
R137	Al ₂ O ₃	68.0	3.0	0.2	Very fine short fibers	
	CaO	12.0				
	SiO ₂	20.0				
R138	Al ₂ O ₃	80.0	2.0	0.2	Very fine short fibers	
	CaO	10.0				
	SiO ₂	10.0				
R139	Al ₂ O ₃	60.0	2	0.5	Very fine short fibers; severe thermal shock	
	CaO	10.0				
	SiO ₂	30.0				
R140	CaF ₂	24.0	0.5	0.3	Very viscous melt; 1/2-2 inch fine fibers	
	SiO ₂	76.0				
R141	CaF ₂	43.0	3.0	1.4	Low viscosity melt; 1-2 inch fine fibers	1530
	SiO ₂	57.0				
R142	CaF ₂	35.0		0	Melted in 1400°C sinter	
	SiO ₂	20.0				
	Al ₂ O ₃	45.0				
R143	CaF ₂	13.0		0	Melted in 1400°C sinter	
	SiO ₂	17.0				
	Al ₂ O ₃	35.0				
	ZnO	35.0				
R144	SiO ₂	57.3		0	Melted in 1400°C sinter	
	Al ₂ O ₃	7.2				
	MgO	2.4				
	ZrO ₂	28.5				
	Sb ₂ O ₃	4.6				
*Fusion test of glassy pellets.						

Table I (continued). Ceramic fiber compositions.

Composition Number	Material	Weight Percent	Optimum Blast Delay Time Seconds	Fiber Yield Grams per 50 Blasts	Comments	Fusion Temperature °C
R145	SiO ₂	57.7	0.5	1.0	Fine short dark gray fibers	1485
	Al ₂ O ₃	7.2				
	MgO	2.4				
	ZrO ₂	28.7				
	V ₂ O ₅	4.0				
R146	SiO ₂	61.8	0.5	1.4	2-3 inch medium texture fibers	1500
	Al ₂ O ₃	7.7				
	MgO	2.6				
	ZrO ₂	25.9				
	LB-88 *	2.0				
R147	SiO ₂	57.0	1.0	1.8	Somewhat viscous melt; short fine fibers	1500
	Al ₂ O ₃	7.1				
	MgO	2.3				
	ZrO ₂	28.6				
	CoO ₂	5.0				
R148	SiO ₂	57.1		0	Melted in 1400°C sinter	
	Al ₂ O ₃	6.5				
	MgO	2.4				
	ZrO ₂	29.0				
	TiO ₂	5.0				
R149	SiO ₂	24.6	3.0	2.4	Low viscosity high surface tension; 2-3 inch fibers	1500
	Al ₂ O ₃	55.4				
	CaF ₂	20.0				
R150	SiO ₂	21.2	3.0	2.4	Low viscosity high surface tension; 2-3 inch fibers	1520
	Al ₂ O ₃	43.8				
	CaF ₂	10.0				
	ZnO	25.0				
R151	Al ₂ O ₃	40.0		0	Melted in 1400°C sinter	
	P ₂ O ₅	40.0				
	CaO	20.0				
*Glass frit from Glostex Chemical Co., Los Angeles, California.						

Table I (continued). Ceramic fiber compositions.

C. Fiber Evaluation

1. Fiber Tensile Strength

Evaluations of the tensile strengths of nine selected fiber materials were conducted with the improved tensile strength apparatus, Figure 4. In this apparatus a more convenient method of heating and melting the mounting wax was employed which consisted of small individual heaters operated by a treadle. An improved linkage mechanism which prevented shattering of the fiber ends after breakage reduced the "mortality" (aborted test results) from over 90 percent to less than five percent and also somewhat reduced the usual spread of test data.

The results of these tests on the nine fiber materials are presented graphically in Figure 5. Ten specimens were tested for each bar in the figure. The raw fibers with the highest mean-tensile strength was R-141 with a value of 295,000 psi. However, since the two sigma limits of all materials overlap, statistically there is no significant difference in the strengths of the different fibers.

The effects of non-aqueous glass fiber finishes on strength were more apparent. Two groups of freshly made R-74 fibers were treated respectively with one percent Quanta 1025C* in methyl ethyl ketone and with ten percent Linde A-1100** in anhydrous xylene. After immersion the fibers were washed with water to hydrolyze the finishes as prescribed by their manufacturers. The fibers were then dried and evaluated. The results are also shown in Figure 5. The A-1100 finish improved the mean tensile strength of R-74 by 25 percent. The 1025C finish lowered the tensile strength and increased the scattering of data.

To study the effect of time on the strength of fibers, R-74 fibers from a freshly made batch were tested in various time increments over a twelve-day period. In Figure 6 it is seen that the expected sharp decrease in strength with time is not indicated. Significant differences would be noticed, perhaps, with a more precise apparatus.

*Thalco, 6431 Flotilla Street, Los Angeles 22, California.

**Silicones Division, Union Carbide Corporation, 2770 Leonis Blvd., Los Angeles (Vernon) 58, California.

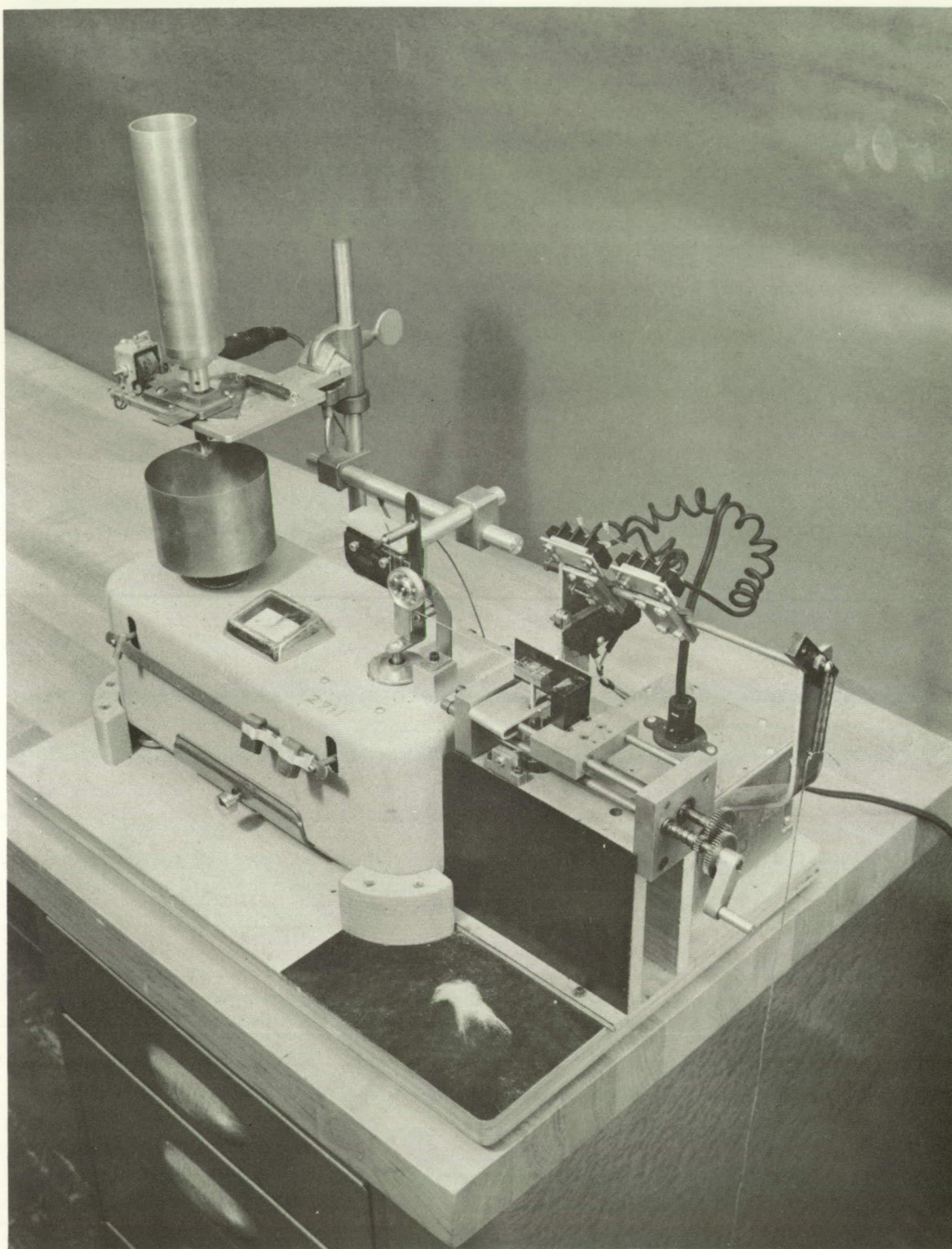


Figure 4. Fiber tensile strength apparatus.

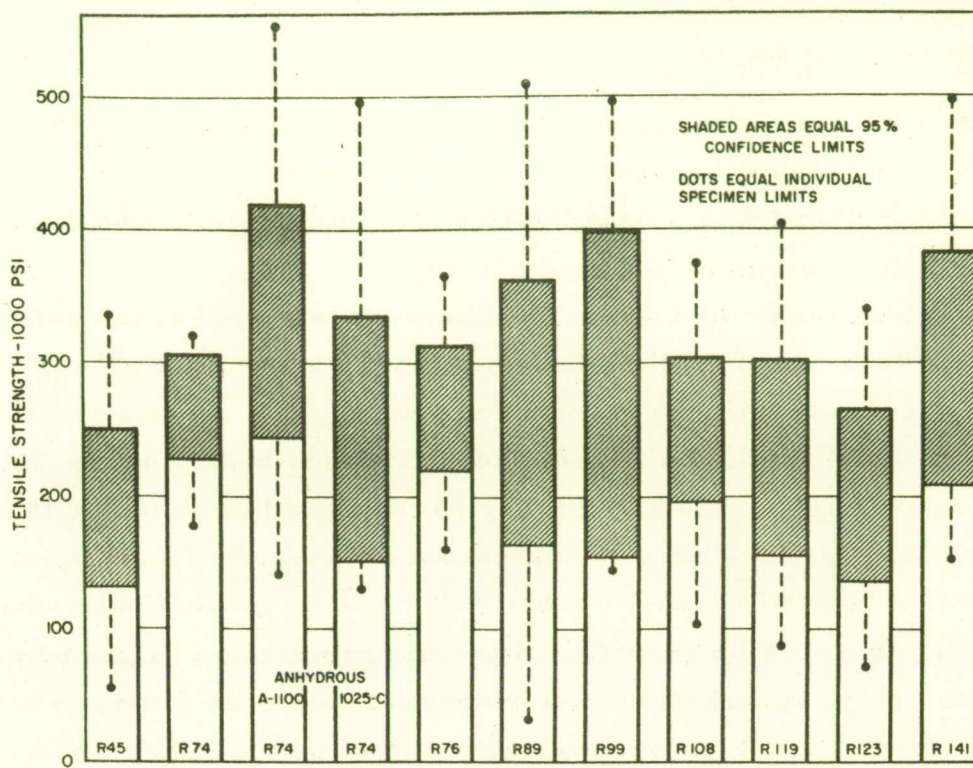


Figure 5. Tensile strengths of selected single fibers.

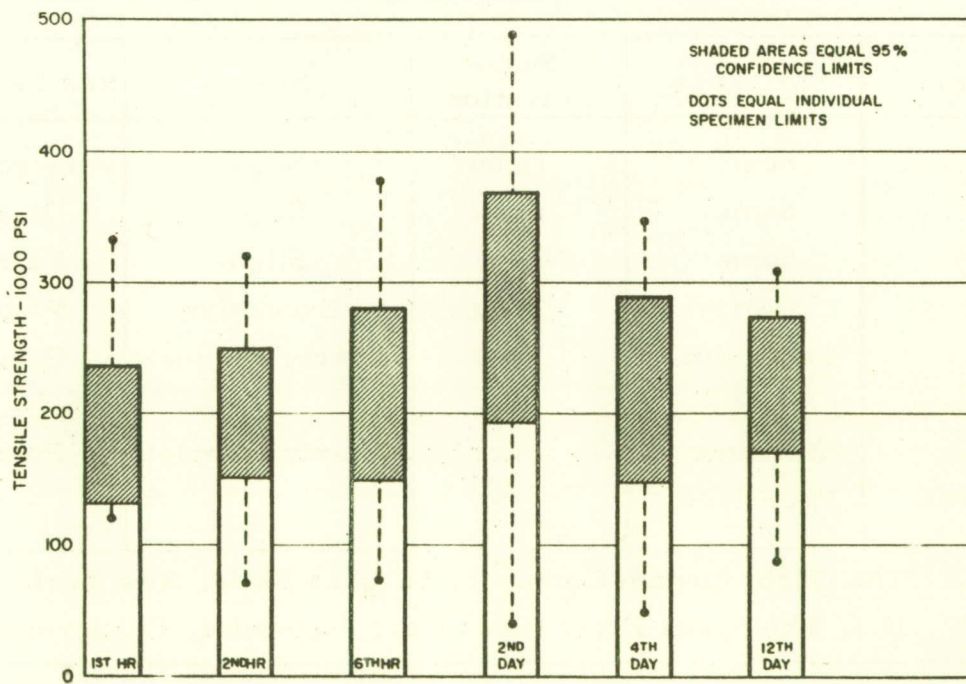


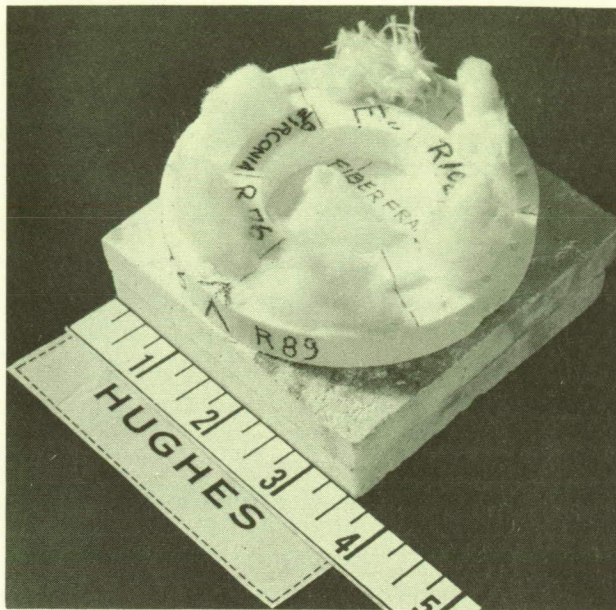
Figure 6. Effect of time on tensile strength of fibers.

2. Static Heat Resistance

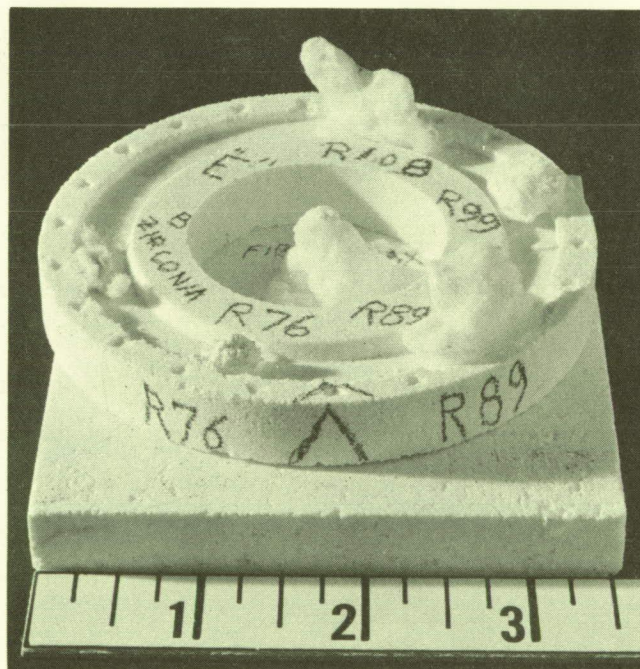
To determine the resistance of various bulk fibers to 2750°F (1510°C) a static heating test was conducted. About one-half gram of depelletized fibers was pressed gently into loose balls about three-fourths inch in diameter and placed on a setter ring, Figure 7, in an oxy-acetylene fusion furnace. The fibers were heated at the rate of about 500°C per hour to 1520°C and the furnace was shut off and permitted to cool normally to room temperature. The results are shown in Figure 7 and are listed in order of decreasing resistance in Table II. The temperature resistance of Fiberfrax appeared to be better than that of R-89 and R-108. This was unexpected because the fusion point of Fiberfrax was 1740°C, or 70°C and 90°C lower, respectively, than R-89 (1810°C) and R-108 (>1830°C). Since the Fiberfrax was placed down inside the ring, apparently it was somewhat sheltered from the same degree of radiant and convective heating to which the other materials were subjected. It is noteworthy that the poorest performer of the refractory fibers tested was zirconia "B" and that "E" glass was completely melted and vaporized.

Fiber	Shrinkage	Shape Retention	Fusion	Resiliency
Fiberfrax ¹	Some	Good	Slight	Very good
R-108	Some	Good	Slight	Good
R-89	Some	Fair	Slight	Fair
R-99	Excessive	Poor	Excessive	Poor
R-76	Excessive	Poor	Nearly complete	Poor
Zirconia "B" ²	Extreme	Poor	Nearly complete	Poor
"E" glass	Vaporized	--	--	--
1. The Carborundum Company, Niagara Falls, New York.				
2. H.I. Thompson Fiber Glass Co., Inglewood, California.				

Table II. Static heat resistance.



Before Test



After Heating to 1510°C (2750°F)

Figure 7. Static heat resistance of ceramic fibers.

D. Fiber-Resin Composites

1. Materials Selected for Composites

The selection of the final fiber compositions for volume fiberizing, felting, and composite fabrication was based on three factors--high yield, high fusion temperature, and, where significant, the type of composition, with emphasis placed on yield because of the larger quantities of samples required for testing in this program. It must be pointed out that this emphasis was necessary because of the inherent volume production limitations of the vertical fiberizing apparatus which was designed only as a research apparatus with flexible operating parameters to accommodate a variety of very different materials. It is understood that an apparatus specifically tailored to a particular composition would produce a much higher fiber yield from that composition. The selected fibers are shown in Table III, which lists composition, yield, and fusion temperature. Fiberfrax was included in the composite tests for a comparison of the new fibers with a typical commercial material.

2. Composite Fabrication

Fiber Cleaning and Felting

A new, more effective method of removing pellets from the blown fibers was developed. About 50 grams of fibers at a time were placed in a glass container closed with porous paper. A low pressure (5 psi) air jet was used to swirl the fibers around inside the container. All pellets but the very smallest were rapidly broken off the fibers, whereupon they settled to the bottom of the container. Each batch of fibers could be depelletized in about five minutes, and the method resulted in a manyfold improvement over the older method of shaking the fibers in a wire basket.

The cleaned fibers were felted with a one-gallon Waring Blendor in forty gram batches. The suspension fluid was 3500 cc of a two percent solution of Linde A-1100 silane finish in water. The blendor was permitted

to agitate the suspension for 2-1/2 minutes at a low speed after which the fibers were poured into a ten-inch Buchner filtering funnel connected to a vacuum pump. The fibers settled on the filter paper and the resulting felt was free of pellets, very uniform in texture and thickness, and the fibers were randomly oriented and well intermeshed in the plane of the felt, Figure 8. Two separate batches of R-74 fibers were treated prior to felting with the two non-aqueous glass fiber finishes previously described.

Composition Number	Fiber Yield gm per 50 Blasts	Fiber Fusion Degrees C	Type of Composition
R45	6.6	1475	Magnesia-Spinel plus Silica
R74	8.6	1450	Magnesia-Alumina-Zirconia Silica
R76	3.2	1605	Magnesia-Alumina-Zirconia Silica
R99	7.0	1580	Magnesia-Alumina-Zirconia Silica
R119	3.4	1575	Magnesia-Alumina-Zirconia Silica
R89	1.5	1810	Zinc-Spinel-Silica
R141	1.4	1530	Calcium-Alumina-Fluoride (no Silica)
R86	1.2	1680	Silica-Zirconia plus Flux
R123	2.2	1575	R76 plus Flux
R108	1.3	1830	Zinc-Spinel plus Silica and Flux

Table III. Fiber compositions selected for composite specimens.



Figure 8. Ceramic fiber felts for composite specimen fabrication.

Impregnation, Molding and Postcuring

The ten-inch felts of the selected fibers (treated with the appropriate fiber finish) were impregnated by soaking them in the following resin solution:

Fibers	70 parts by weight
CTL 91-LD resin	43 parts by weight of 70 percent varnish
Acetone	43 parts by weight

The 43 parts by weight of 70 percent varnish is the equivalent of 30 parts by weight of resin solids. The 70-30 fiber-resin ratio was selected because of the improved high temperature performance of composites made with a lower resin content. The impregnated felts were dried for three hours at 90°C, after which two-inch disc and one inch by eight inch bar premold specimens were cut from the felts. The premold specimens were then placed in the appropriate dies and molded as follows:

<u>Die</u>	<u>Die Temperature</u>	<u>Molding Time</u>	<u>Total Pressure</u>
2 inch disc	150°C	60 minutes	4 tons
1 inch by 8 inch bar	150°C	60 minutes	10 tons

The specimens were postcured according to a programmed heating cycle as follows: maintain specimens 18 hours at 275°F, increase temperature gradually in 42 hours to 400°F, maintain four hours at 400°F.

3. Composite Evaluation

All strength testing was conducted at room temperature with a Baldwin-Tate-Emery Testing Machine. Flexural strength tests were performed according to the ASTM D790-58T test procedure using a test specimen of approximately 0.1 × 0.5 × 4 inches, and a test span of two inches. The results given in Table IV are the average values of the number of specimens indicated for each fiber composite material. The modulus of elasticity in flexure is also reported. The punch shear tests were conducted with the 2-inch discs according to the ASTM D732-46 testing procedure. The results are also given in Table IV.

Specimen Number	Fiber	Finish	Flexural Strength psi	Average Flexural Strength	Modulus of Elasticity in Flexure psi $\times 10^6$	Average Modulus of Elasticity psi $\times 10^6$	Punch Shear Strength psi
1	R74	Aqueous A-1100	15,650	19,958	1.65	1.86	10,415
2			20,600		1.91		
3			21,300		1.54		
4			17,850		1.34		
5			20,250		1.93		
6			19,900		2.22		
7			24,300		2.04		
8			21,200		2.23		
9			22,700		1.83		
10			18,850		1.97		
11			20,200		2.15		
12			16,700		1.56		
13	R74	10% A-1100 in xylene	19,950	18,616	1.66	1.69	9,682
14			16,700		1.71		
15			18,250		1.83		
16			19,550		1.57		
17	R74	1% 1025 C in M. E. K.	19,900	16,437	1.51	1.46	7,855
18			15,400		1.50		
19			17,150		1.47		
20			13,300		1.37		
21	R99	Aqueous A-1100	12,100	13,231	1.36	1.28	9,559
22			17,900		1.34		
23			11,400		1.12		
24			8,750		1.11		
25			11,450		1.26		
26			12,750		1.36		
27			15,050		1.36		
28			16,450		1.32		
29	R89	Aqueous A-1100	14,600	14,738	1.37	1.54	11,509
30			10,000		1.16		
31			13,300		1.39		
32			14,800		1.16		
33			17,700		1.87		
34			15,100		1.78		
35			16,000		1.87		
36			16,400		1.69		

Table IV. Strength of ceramic fiber 91-LD resin composites.

Specimen Number	Fiber	Finish	Flexural Strength psi	Average Flexural Strength	Modulus of Elasticity in Flexure psi $\times 10^6$	Average Modulus of Elasticity psi $\times 10^6$	Punch Shear Strength psi
37	R45	Aqueous A-1100	19,700	17,125	1.46	1.23	7,447
38			16,700		1.46		
39			14,550		1.34		
40			15,650		1.09		
41			12,200		0.87		
42			18,800		1.19		
43			13,200		1.16		
44			15,600		0.85		
45			13,700		1.47		
46			7,550		1.14		
47	R76	Aqueous A-1100	14,100	17,350	1.45	1.77	8,931
48			12,700		1.24		
49			17,800		2.11		
50			14,500		1.63		
51			20,800		1.49		
52	R119	Aqueous A-1100	16,300	17,993	1.87	1.75	8,715
53			17,650		1.57		
54			15,000		1.58		
55			18,150		1.75		
56			18,350		1.57		
57			20,100		1.86		
58			15,200		1.98		
59			21,400		1.85		
60			19,100		1.85		
61			13,850		1.07		
62	R123	Aqueous A-1100	20,650	18,150	1.70	1.36	--
63			19,950		1.30		
64			12,200		1.42		
65			12,200		1.44		
66			12,000		1.42		
67			10,600		1.16		
68			10,200		1.54		
69			12,000		1.54		
70			12,900		1.57		
71			11,200		1.71		
	Fiberfrax	Aqueous A-1100		11,662	1.52	1.66	8,352

Table IV (continued). Strength of ceramic fiber 91-LD resin composites.

It is seen that R-74 has the highest average flexural strength, 19,958 psi, and that R-89 has the highest punch shear strength, 11,509 psi. This does not agree with the single fiber tensile strengths reported for these materials, Figure 5. The effects of anhydrous finishes are not clearly indicated and do not agree with the single fiber tensile strengths.

Plasma arc tests were conducted on composite specimens as shown in Table V. The heat flux was 550 BTU/foot²-sec. It is seen that most specimens had a fairly uniform ablation rate of 0.011 to 0.016 inch per second. The composites containing R-99 fibers had the lowest ablation rate, 0.010 and 0.006 inch per second. The ablation rates of these materials agree with a value of 0.013 inch per second for Fiberglas-Micarta No. 259-2 as reported by the Engineering Experiment Station at Georgia Tech.

Test No.	Fiber	Composition Weight %		Specimen Thickness		Burn Depth Inch	Test Duration Seconds	Ablation Rate Inch/second
		Fiber	91-LD Resin	Before Exposure Inch	After Exposure Inch			
1	R-45	64.4	35.6	0.202	0	0.202	15	0.013
2	R-45	62.5	37.5	0.191	0	0.191	15	0.013
3	R-74	64.1	35.9	0.133	0	0.133	10	0.013
5	R-74	64.6	35.4	0.135	0	0.135	9	0.015
6	R-74	60.5	39.5	0.165	0	0.165	12	0.014
7	R-74	50.8	49.2	0.152	0	0.152	11	0.014
8	R-76	63.6	36.4	0.162	0	0.162	11	0.015
9	R-76	68.1	31.9	0.187	0.045	0.142	10	0.014
10	R-89	56.5	43.5	0.166	0	0.166	12	0.014
11	R-89	57.1	42.9	0.162	0.040	0.122	11	0.011
12	R-99	61.9	38.1	0.169	0.050	0.119	12	0.010
13	R-99	65.9	34.1	0.186	0.120	0.066	10	0.006
14	R-119	62.5	37.5	0.185	0.064	0.121	15	0.008
15	R-119	64.3	35.7	0.194	0.025	0.169	11	0.016
16	R-123	71.5	28.5	0.078	0	0.078	6	0.013
17	Fiber-frax	73.0	27.0	0.254	0.069	0.185	15	0.012

Table V. Plasma arc tests on fiber-resin composites.

E. Ceramic Fiber Yarns and Fabrics

Preliminary studies for processing fibers into yarn and fabric were conducted with R-99 fibers. These fibers were very long, uniform and flexible and appeared to have a degree of interattraction which aided somewhat in handling. By adjusting the delay time fibers of various lengths and diameters were produced. The fibers were well cleaned of pellets and treated with five percent aqueous solutions of several different gums and water soluble waxes. Attempts to card both dry and moist fibers with conventional hand cards were unsuccessful due to the brittleness of the fibers. The moist fibers were hand pulled into strands, twisted into 1/8-inch yarns several inches in length, and allowed to dry. The gums were slightly more effective in improving the handling characteristics. The yarns were relatively strong and flexible, particularly those made with the finer fibers. Several moist yarns were hand woven into a crude fabric swatch. Though very elementary, these studies indicate the practicality of processing staple ceramic fibers into fabrics.

F. Selection of Ceramic Fiber Compositions for Further Studies

In this program, 25 materials were developed which have promising characteristics. These materials, listed in Table VI all have fiber yields of at least one gram per fifty blasts and fusion temperatures of at least 1450°C with the fusion temperatures of three materials exceeding 1800°C. With these 25 materials combinations of a variety of fiber characteristics are manifested such as fiber length and diameter, relative brittleness, melting behavior (surface tension and viscosity), and resistance to devitrification. Several fiber compositions are superior as reinforcements in resin composites (e.g. R-74 and R-89) and others appear to be more suitable for fabrics (e.g. R-99). Satisfactory fiber forming abilities of the 25 compositions have been demonstrated in the vertical arc fiberizing apparatus. It is considered practical to produce larger quantities of fibers by other fiberizing methods from any of these materials as required for yarn and fabric processing.

Composition Number	Composition		Fiber Yield Gm per 50 Blasts	Fiber Fusion Temperature °C
	Material	Percent		
R45	SiO ₂	36.00	6.6	1475
	Al ₂ O ₃	48.00		
	MgO	16.00		
R58	SiO ₂	25.00	3.0	1495
	Al ₂ O ₃	56.00		
	MgO	19.00		
R59	SiO ₂	35.50	5.8	1450
	Al ₂ O ₃	30.50		
	MgO	9.50		
	ZrO ₂	24.50		
R66	SiO ₂	42.75	1.4	1500
	Al ₂ O ₃	15.25		
	MgO	4.75		
	ZrO ₂	37.25		
R74	SiO ₂	50.00	8.6	1450
	Al ₂ O ₃	22.50		
	MgO	7.50		
	ZrO ₂	20.00		
R76	SiO ₂	60.00	3.2	1605
	Al ₂ O ₃	7.50		
	MgO	2.50		
	ZrO ₂	30.00		
R79	SiO ₂	20.00	3.0	1550
	Al ₂ O ₃	45.00		
	MgO	15.00		
	ZrO ₂	20.00		
R86	SiO ₂	45.00	1.2	1680
	ZrO ₂	45.00		
	PbO	10.00		
R87	SiO ₂	40.00	2.0	1680
	ZrO ₂	40.00		
	ZnO	20.00		
R89	SiO ₂	35.00	1.5	1810
	Al ₂ O ₃	32.50		
	ZnO	32.50		
R91	SiO ₂	25.00	2.0	1620
	Al ₂ O ₃	62.50		
	MgO	12.50		
R99	SiO ₂	50.00	7.0	1580
	Al ₂ O ₃	27.00		
	MgO	3.00		
	ZrO ₂	20.00		
R108	SiO ₂	17.90	1.3	> 1830
	Al ₂ O ₃	35.70		
	ZnO	35.70		
	Sb ₂ O ₃	10.70		

Table VI. Fiber compositions selected for further study.

Composition Number	Composition		Fiber Yield Gm per 50 Blasts	Fiber Fusion Temperature °C
	Material	Percent		
R110	SiO ₂	18.50	1.2	1830
	Al ₂ O ₃	37.00		
	ZnO	37.00		
	Sa ₂ O ₃	7.50		
R112	SiO ₂	17.90	1.4	1750
	Al ₂ O ₃	35.70		
	ZnO	35.70		
	CeO ₂	10.70		
R113	SiO ₂	18.50	1.6	1750
	Al ₂ O ₃	37.00		
	ZnO	37.00		
	Y ₂ O ₃	7.50		
R117	SiO ₂	54.50	1.0	1505
	Al ₂ O ₃	6.83		
	MgO	2.27		
	ZrO ₂	27.20		
	P ₂ O ₅	9.20		
R119	SiO ₂	60.00	3.4	1575
	Al ₂ O ₃	10.00		
	ZrO ₂	30.00		
R123	SiO ₂	58.20	2.2	1575
	Al ₂ O ₃	7.28		
	MgO	2.42		
	ZrO ₂	29.20		
	Sa ₂ O ₃	2.90		
R132	SiO ₂	45.00	1.2	1790
	Al ₂ O ₃	40.00		
	P ₂ O ₅	15.00		
R141	Al ₂ O ₃	57.00	1.4	1530
	CaF ₂	43.00		
R145	SiO ₂	57.70	1.0	1485
	Al ₂ O ₃	7.20		
	MgO	2.40		
	ZrO ₂	28.70		
	V ₂ O ₅	4.00		
R147	SiO ₂	56.96	1.8	1500
	Al ₂ O ₃	7.08		
	MgO	2.36		
	ZrO ₂	28.60		
	CeO ₂	5.00		
R149	SiO ₂	24.60	2.4	1500
	Al ₂ O ₃	55.40		
	CaF ₂	20.00		
R150	SiO ₂	21.20	2.4	1520
	Al ₂ O ₃	43.80		
	CaF ₂	10.00		
	ZnO	25.00		

Table VI (continued). Fiber compositions selected for further study.

IV. PERSONNEL

The personnel of the Ceramics Development Group assigned to this project are listed below:

L. E. Gates	Member of Technical Staff	Project Head
W. E. Lent	Associate Engineer	Fiberizing Studies Composition Studies and Fiber Evaluation
W. T. Teague	Member of Technical Staff	Reports and Composite Testing
A. A. Curme	Research Assistant	Fiber Tensile Strength Testing
A. M. Dowell	Member of Technical Staff	Composite Testing
M. Hisashima	Laboratory Analyst	Fiber Production

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